

## A. RESEARCH TASK:

Thermal Emission Spectroscopy of the Middle Atmosphere

## B. INVESTIGATORS AND INSTITUTIONS

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## C. RESEARCH OBJECTIVES

The general objective of this research is to obtain, via remote sensing, simultaneous measurements of the vertical distributions of stratospheric temperature, ozone, and trace constituents that participate in the catalytic destruction of ozone ( $\text{NO}_y$ :  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{HNO}_3$ ,  $\text{ClONO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_4$ ;  $\text{Cl}_x$ :  $\text{HOCl}$ ), and the source gases for the catalytic cycles ( $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCI}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHF}_2\text{Cl}$ , etc.). Data are collected during a complete diurnal cycle in order to test our present understanding of ozone chemistry and its associated catalytic cycles. The instrumentation employed is an emission-mode, balloon-borne, liquid-nitrogen-cooled Michelson interferometer-spectrometer (SIRIS), covering the mid-infrared range with a spectral resolution of  $0.020 \text{ cm}^{-1}$ . Cryogenic cooling combined with the use of extrinsic silicon photoconductor detectors allows the detection of weak emission features of stratospheric gaseous species. Vertical distributions of these species are inferred from scans of the thermal emission of the limb in a sequence of elevation angles.

## D. SUMMARY OF PROGRESS AND RESULTS

The fourth SIRIS balloon flight was carried out from Palestine, Texas on September 15-16, 1986 with 9 hours of nighttime data (40 km). High quality data, with spectral resolution  $0.022 \text{ cm}^{-1}$ , were obtained for numerous limb sequences. Fifteen stratospheric species have been identified to date from this flight: five species from the  $\text{NO}_y$  family ( $\text{HNO}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{ClONO}_2$ ,  $\text{N}_2\text{O}_5$ ), plus  $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CHF}_2\text{Cl}$ ,  $\text{CF}_4$ , and  $\text{CCl}_4$ . The nighttime values of  $\text{N}_2\text{O}_5$ ,  $\text{ClONO}_2$ , and total odd nitrogen have been measured for the first time, and compared to model results. Analyses of the diurnal variation of  $\text{N}_2\text{O}_5$  within the 1984 and 1986 data sets, and of the 1984  $\text{ClONO}_2$  measurements, were presented in the literature.

The demonstrated ability of SIRIS to measure all the major  $\text{NO}_y$  species, and therefore to determine the partitioning of the nitrogen family over a continuous diurnal cycle, is a powerful tool in the verification and improvement of photochemical modeling.

## E. JOURNAL PUBLICATIONS

(1) J.C. Brasunas et al., "Balloon-borne cryogenic spectrometer for measurement of lower stratospheric trace constituents," Cryogenic Optical Systems and Instruments II, Ramsey K. Melugin (Ed.), Proc. SPIE 619, 80-88, 1986.

- (2) V.G. Kunde et al., "Infrared spectroscopy of the lower stratosphere with a balloon-borne cryogenic Fourier spectrometer," Applied Optics, 26, 595, 1987.
- (3) M.M. Abbas et al., "Simultaneous Measurement of Stratospheric  $O_3$ ,  $H_2O$ ,  $CH_4$ , and  $N_2O$  Profiles From Infrared Limb Thermal Emissions," J.G.R., 92, 8343, 1987.
- (4) S.T. Massie et al., "Atmospheric Infrared Emission of  $ClONO_2$  Observed by a Balloon-Borne Fourier Spectrometer," J.G.R., 92, 14806, 1987.
- (5) W. Shaffer et al., "Retrieval of Constituent Mixing Ratios from Thermal Emission Spectra," Applied Optics, 27, 3482, 1988.
- (6) J.C. Brasunas et al., "Cryogenic Fourier spectrometer for measuring trace species in the lower stratosphere," Applied Optics, 27, 4964, 1988.
- (7) V.G. Kunde, et al., "Measurement of nighttime stratospheric  $N_2O_5$  from infrared emission spectra, G.R.L., 15, 1177, 1988.
- (8) W.C. Maguire et al., "Infrared emission high spectral resolution atlas of the stratospheric limb," Applied Optics, 28, 1048, 1989.

## **Measurement of HO<sub>2</sub> and Other Trace Gases in the Stratosphere Using a High Resolution Far-Infrared Spectrometer at 28 km**

### **Investigators and Institutions:**

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### **Abstract of Research Objectives:**

This research aims to measure the stratospheric concentration profiles of a number of trace gases involved in ozone photochemistry, using a high resolution Fourier transform spectrometer, telescope, and stabilized pointing system (the FIRS-2 system) on a high altitude balloon platform. Spectra are obtained at 0.004 cm<sup>-1</sup> resolution in the far-infrared (70-220 cm<sup>-1</sup>) and the mid-infrared (350-700 cm<sup>-1</sup>), using the thermal emission of the atmosphere itself as the spectral source. The research includes balloon flights with multi-instrumented gondolas, with the objectives of increasing the number of simultaneously-measured, related species, and of providing cross-checks among different measurement techniques.

### **Summary of Progress and Results:**

There have been three successful balloon flights of the FIRS-2 system, taking place in October 1987, May 1988, and May 1989. The latter two flights also included the Jet Propulsion Laboratory (JPL) FILOS instrument, which measures stratospheric OH and several other species, on the gondola. A flight is currently scheduled for September 1989 including FIRS-2, FILOS, and the JPL BMLS instrument (for measuring ClO) on the same gondola. The purpose of this flight is to obtain measurements simultaneous in time and space of ClO, HO<sub>2</sub>, and HOCl, as a test of their close chemical relationship, in addition to our usual species measurements.

Atmospheric molecules detected to date in spectra from FIRS-2 balloon flights include OH, HO<sub>2</sub>, H<sub>2</sub>O (including minor isotopic species and vibrational hot bands), O(<sup>3</sup>P), O<sub>2</sub> (including minor isotopic species), O<sub>3</sub> (including minor isotopic species and vibrational hot bands), HCl, HF, HOCl, NO<sub>2</sub>, N<sub>2</sub>O, HNO<sub>3</sub> and CO<sub>2</sub>.

We have used FIRS-2 balloon flight spectra to obtain the first measurement of stratospheric HOCl, including altitude profiles and their diurnal variation. We have made very accurate determinations of the altitude profile of HO<sub>2</sub>, including nighttime measurements and upper limits.

### **Publications:**

Measurement of Stratospheric HOCl: Concentration Profiles, Including Diurnal Variation, K. V. Chance, D. G. Johnson, and W. A. Traub, *Journal of Geophysical Research* 94, 11,059-11,069, 1989.

Ozone Measurements During the Balloon Intercomparison Campaign, D. Robbins, J. Waters, P. Zimmerman, R. Jarnot, J. Hardy, H. Pickett, S. Pollitt, W. Traub, K. Chance, N. Louisnard, W. Evans, and J. Kerr, *Journal of Atmospheric Chemistry*, in press, 1989.

Intercomparison of Measurements of Stratospheric Hydrogen Fluoride, W. G. Mankin, M. T. Coffey, K. V. Chance, W. A. Traub, B. Carli, A. Bonetti, I. G. Nolt, R. Zander, D. W. Johnson, G. Stokes, C. B. Farmer, and R. K. Seals, *Journal of Atmospheric Chemistry*, in press, 1989.

Intercomparison of Stratospheric Water Vapor Profiles Obtained During the Balloon Intercomparison Campaign, D. G. Murcray, A. Goldman, J. Kusters, R. Zander, W. Evans, N. Louisnard, C. Alamichel, M. Bangham, S. Pollitt, B. Carli, B. Dinelli, S. Piccioli, A. Volboni, W. A. Traub, and K. Chance, *Journal of Atmospheric Chemistry*, in press, 1989.

Balloon Intercomparison Campaign: Results of Remote Sensing Measurements of HCl, C. B. Farmer, B. Carli, A. Bonetti, M. Carlotti, B. M. Dinelli, H. Fast, N. Louisnard, C. Alamichel, W. Mankin, M. Coffey, I. G. Nolt, D. G. Murcray, A. Goldman, G. Stokes, D. Johnson, W. Traub, K. Chance, R. Zander, L. Delbouille, and G. Roland, *Journal of Atmospheric Chemistry*, in press, 1989.

Stratospheric Hydroperoxyl Measurements, W. A. Traub, D. G. Johnson, and K. V. Chance, submitted for publication.